AD-A257 410

Marlow Industries, Inc.

Thermoelectric Innovation Through Research

16 October 1992

Defense Documentation Information Center
ATTN: DTIC-DDA
Cameron Station, Bldg 5
Alexandria, VA 22314

Please find enclosed a copy of the final report for the Army SBIR Phase I program on *Resonant Doped Bismuth Telluride for Reliable, Efficient Cryocooling,* (Contract DAAB07-.92-C-K756).

Sincerely,

DTIC
ELECTE
OCT 28 1992
E

E. H. Volckmann
Principal Investigator
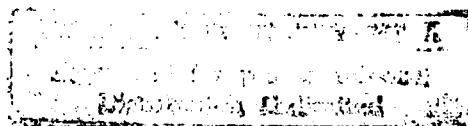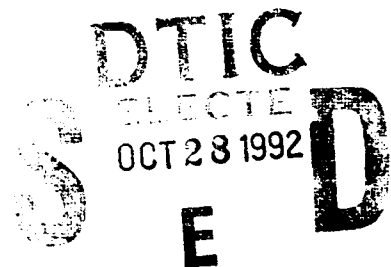
92-28122

10451 Vista Park Road • Dallas, Texas 75238-1645

TEL 214/340-4900 • FAX 214/341-5212

Resonant Doped Bismuth Telluride for Reliable, Efficient Cryocooling

Army SBIR Phase I

Contract DAAB07-.92-C-K756

Final Report

Principal Investigator: E. H. Volckmann

16 October 1992

This Document is Unclassified

Distribution Statement A. Approved for public release; distribution is unlimited.

Introduction

Today's cryogenic coolers that operate down to 77 K suffer from several problems. Their most serious difficulties are significant noise levels, excessive vibration and poor reliability. Thermoelectric coolers do not suffer any of these concerns. However, thermoelectric coolers are not presently capable of cooling to temperatures as low as 77 K. Development of thermoelectric materials capable of extending cooler performance to these temperatures would open up potential applications such as cryogenic cooling of infrared detectors and CCDs as well as removing heat from Joule-Thomson refrigerators.

Presently, the best thermoelectric materials over the temperature range 200 K to 450 K, and the most practical below 200 K, are solid solutions of Bi_2Te_3, Sb_2Te_3 and/or Bi_2Se_3. These alloys yield a peak dimensionless figure of merit, ZT, of approximately one near 300 K. These materials often require doping in order to optimize the carrier concentration and figure of merit, Z. As reported by Ravich and Vedernikov[1], certain impurities can also be added to improve thermoelectric properties through a selective scattering mechanism.

The Ravich and Vedernikov review paper discusses work in which the Z of PbTe was dramatically improved upon the addition of Na and Tl together. PbTe is used as a thermoelectric power generator material typically over the temperature range of 500 K to 800 K. While performance improvements were not significant over this temperature range, it was reported that the Z at 300 K for PbTe, containing both Na and Tl additions, was two to three times higher than samples doped with a single element to the same carrier concentration. The improvement in the Z of PbTe, upon addition of the two impurities, is attributed to resonance charge carrier scattering.

Charge carrier scattering is typically viewed as an event which has an adverse effect on thermoelectric properties. It can be shown that the product,

$$\mu(m^*)^{3/2} \, .$$

(1)

where μ =   carrier mobility
          m^* =   carrier effective mass,

should be maximized as one of the requirements for good thermoelectric materials. These two parameters are not independent as μ decreases with increasing m^* because of charge carrier scattering. The carrier mobility is a function of the free path length of the charge carriers between scattering events as the carriers travel through the solid. Scattering events which act to deflect carriers include interactions with:

- the crystal lattice
- impurity atoms
- crystal defects
- other charge carriers

In general, scattering results in a lower μ and therefore lower thermoelectric properties. However, <u>resonance</u> charge carrier scattering is a selective scattering mechanism that can actually improve the thermoelectric properties of a material.

Equation 2 defines Z as a function of the measurable properties α, σ, and κ.

$$Z = \frac{\alpha^2 \sigma}{\kappa}$$

(2)

where α is the Seebeck coefficient
          σ is the electrical conductivity
          κ is the thermal conductivity

It is clear from this equation that $\alpha^2 \sigma$ should be maximized and κ minimized to realize an increase in Z.

3

Resonance charge carrier scattering is accomplished when an impurity is added to the semiconductor and two criteria are met. First, new energy states must be created that result in a broadening of the allowable electron energy state range. Second, these newly created energy levels must be in close enough proximity to the Fermi energy to ensure that a significant quantity of electrons will occupy these states. If these criteria are met α will increase since it is a function of the change in carrier energy between the hot junction and the cold junction. However, the impurity addition also results in carrier scattering which decreases μ as discussed above. This causes a decrease in σ (and a less significant decrease in κ).

The net change in Z can be significant. As mentioned above, Ravich and Vedernikov reported that the Z at 300 K of PbTe increased by a factor of two to three when resonance charge carrier scattering occurred. The objective of the Phase I effort was to demonstrate the feasibility of using the same mode of scattering to improve the thermoelectric properties of Bi_2Te_3 based alloys.

Description of Research

The approach used to demonstrate resonance charge carrier scattering was to first identify an impurity which might create energy levels suitable for an enhancement of α, then synthesize samples at various impurity and carrier concentrations to observe this enhancement.

A Bi_2Te_3 based alloy was chosen as the material to work with because it is the best thermoelectric material system over the temperature range of 200 K to 450 K. Any improvements made to the thermoelectric properties in this temperature range would have immediate significance. The actual Bi_2Te_3-Bi_2Se_3 alloy used, in these experiments, is typically doped with a halogen donor to yield an n type semiconductor with an optimum carrier concentration. Based on the review paper discussion of Ravich and Vedernikov, indium (In) was selected as the impurity to create the desired resonant energy states.

The technical work executed in Phase I can be broken down into three parts:

• determination of In solubility in the Bi-Te-Se alloy

• establishment of the relationship between α and σ for the Bi-Te-Se alloy by varying the bromine (Br) concentration

• search for α enhancement due to resonance charge carrier scattering by varying In and Br concentrations

Since it is very unlikely that an In rich second phase would contribute to good thermoelectric properties, the first task of Phase I was to set the upper concentration limit of In in the Bi-Te-Se alloy. This was accomplished by determining the In solubility limit in the alloy for the growth conditions used.

Samples were prepared by the vertical Bridgman technique. To determine if a second phase had precipitated out of solution, sections were cut from several locations along the length of an ingot. These sections were polished and observed under the metallograph and in the scanning electron microscope. Energy dispersive X-ray analysis was used to qualitatively determine composition and verify the presence of second phase regions. The medium gray regions (see arrows) in figure 1 are In rich second phase. Figures 2 and 3 are spectra from the Bi_2Te_3 based alloy and the In rich second phase respectively. It appears that the second phase is an In-Se compound.
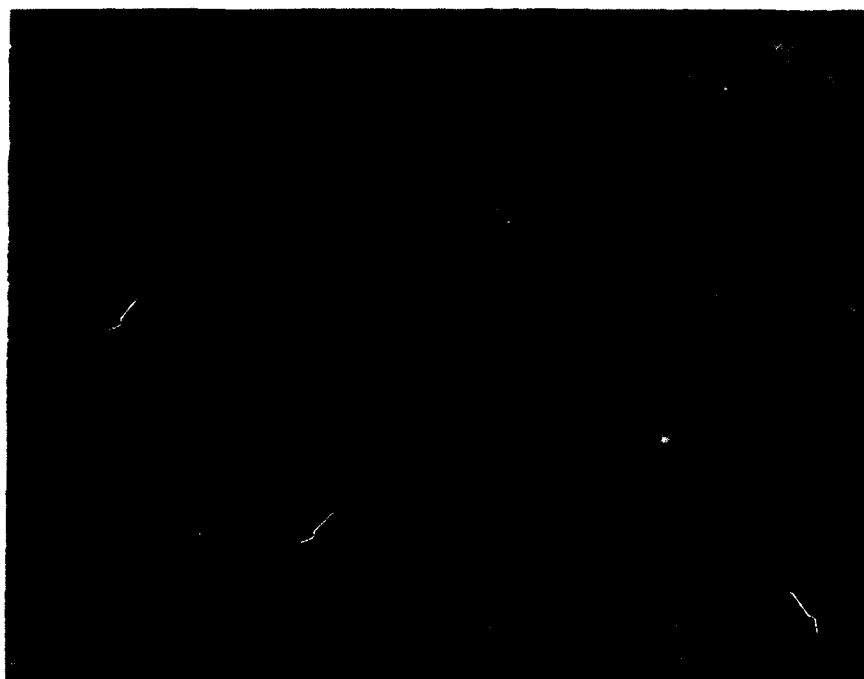
Figure 1. Bi-Te-Se alloy with 5 atomic % In. Arrows point out In-rich second phase. Black areas are porosity. (metallograph, 50X)
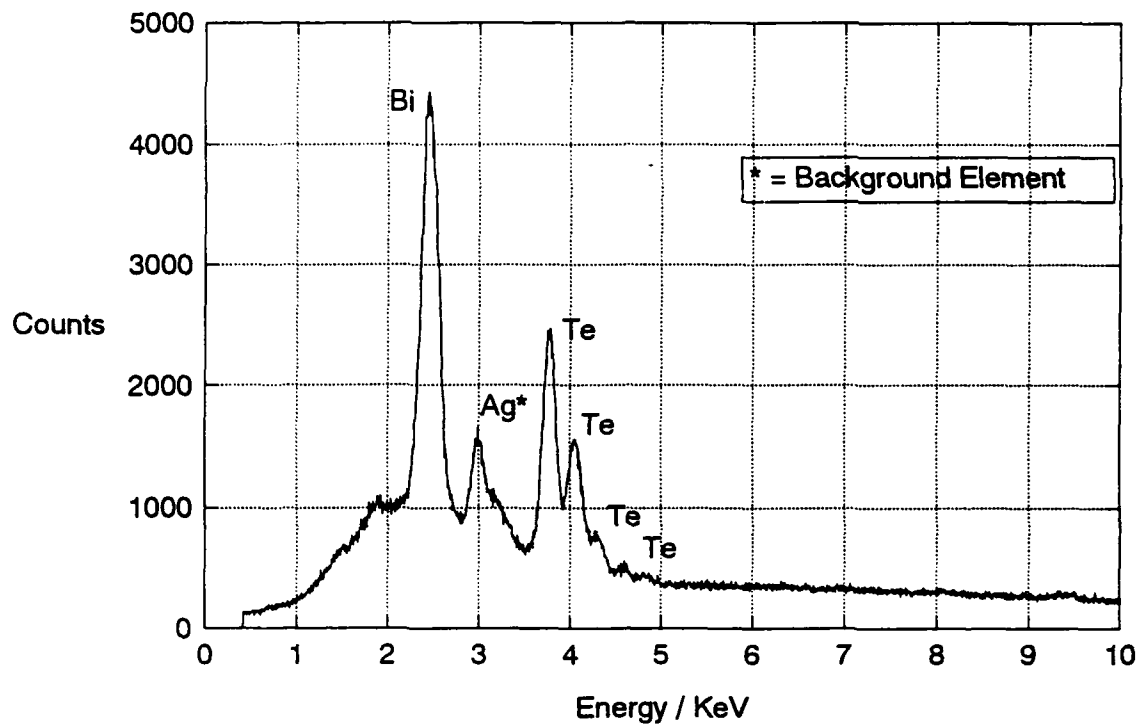
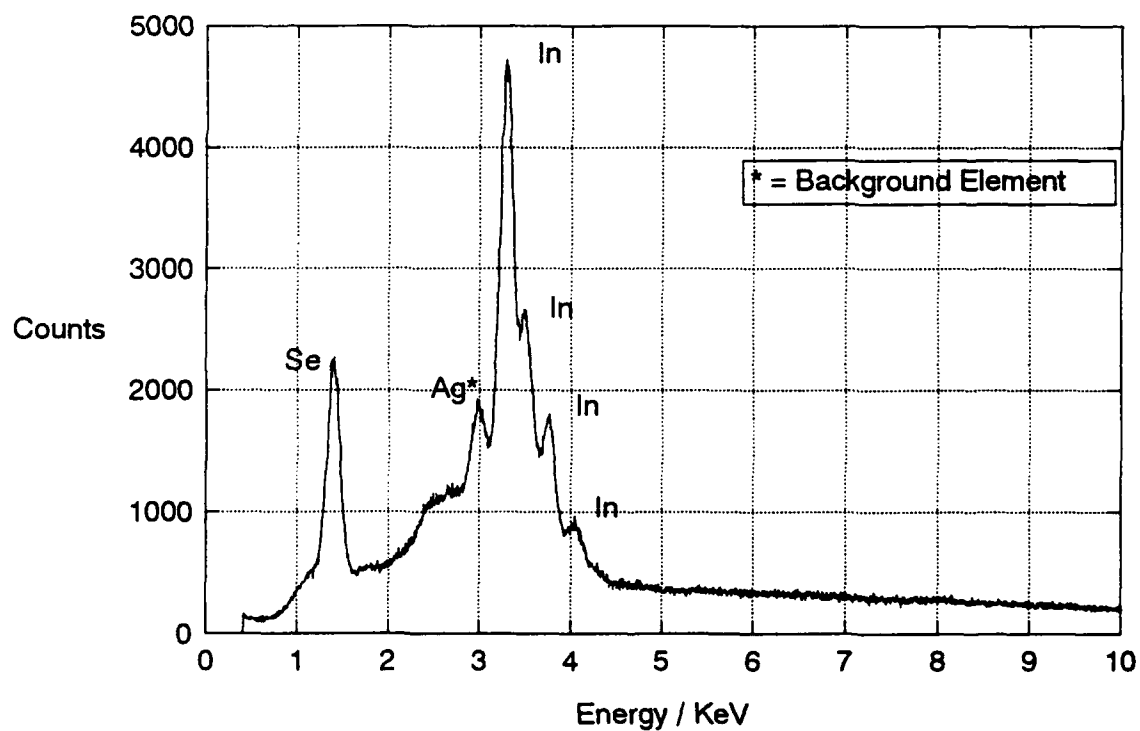**Figure 2**. Bi-Te-Se alloy with 1.7 atomic % In.

Figure 3. In-Se second phase in Bi-Te-Se alloy with 1.7 atomic % In.

7

The resistivity profiles of the In doped ingots were measured and are presented in figure 4. For very low In concentrations the material is a p type semiconductor. This is because the Bi-Te-Se alloy does not solidify stoichiometrically and the resulting point defects behave as acceptors. Higher percentages of In cause the material to become n type. This behavior is not surprising since In acts as a donor impurity in both Bi_2Te_3 and Bi_2Se_3. Rosenberg and Strauss[2] concluded that when In is added to Bi_2Te_3 it either replaces Bi or it replaces Te with Te simultaneously replacing Bi. Horak et al.[3] argue that incorporation of In into Bi_2Se_3 leads to the suppression of the anti-site defect, where Bi atoms are found on Se sites in the atomic lattice. While the specific mechanism(s) of In incorporation into the lattice may not be firmly established yet, it is clear that In behaves as a donor impurity over the concentrations used in phase I.
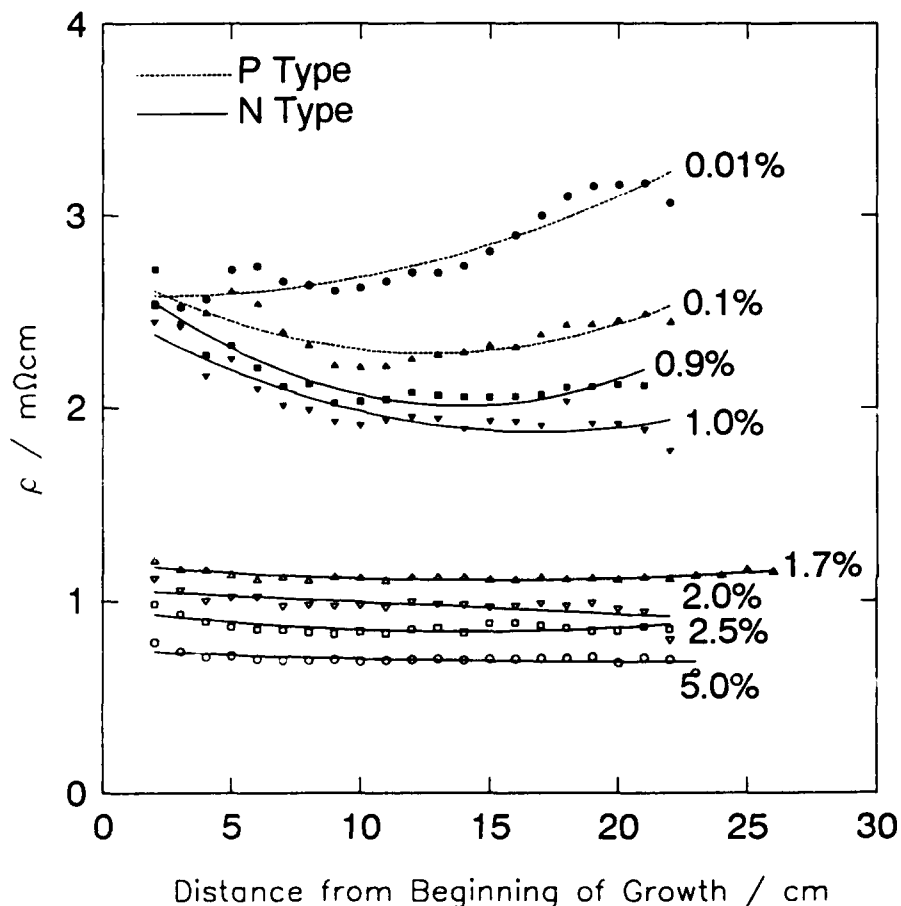

Figure 4. Resistivity profiles for Bi-Te-Se alloy ingots as a function of In addition (atomic %).

Next, to establish a baseline relationship between α and σ, a series of Bi-Te-Se alloy ingots with varying amounts of Br were grown. The resistivity profiles of these ingots are given in figure 5. A Br concentration somewhere between 20 and 50 percent of typical is enough of the donor to cause the Bi-Te-Se alloy to become an n type semiconductor.

Several samples were cut from each ingot. The samples were characterized using a modified Harman method allowing the determination of α, σ and κ. A Jonker plot, α vs logσ, was constructed to graphically present the data; See figure 6.
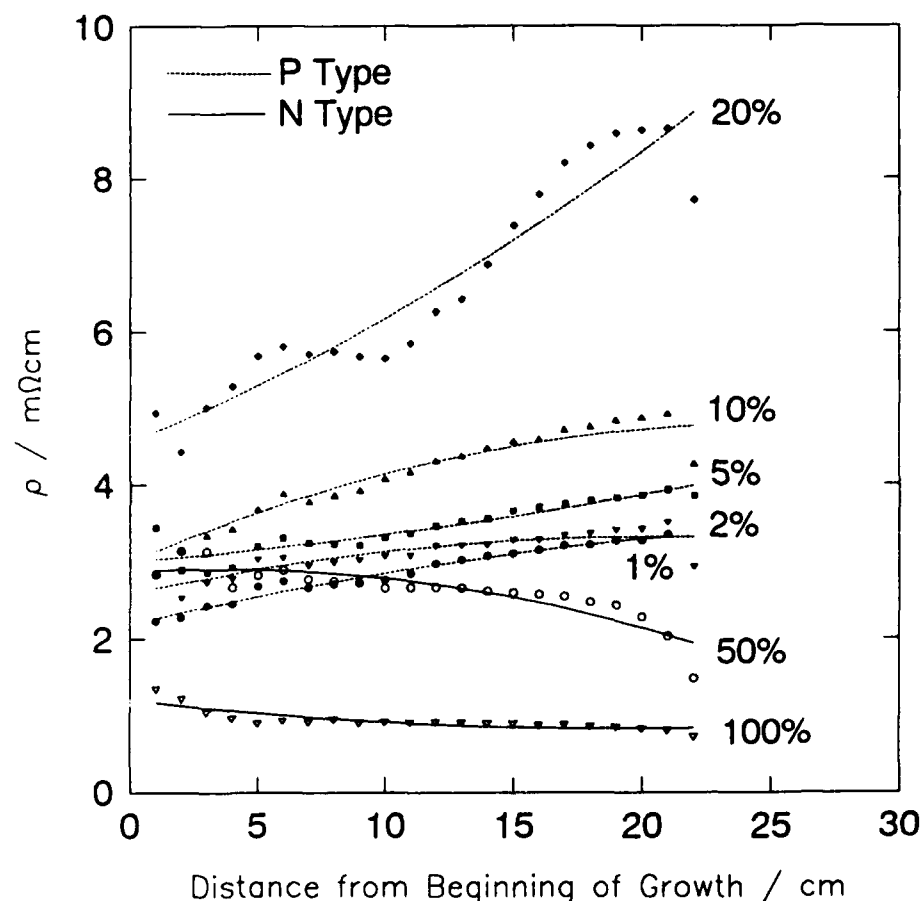

Figure 5. Resistivity profiles for Bi-Te-Se alloy ingots as a function of Br addition (% of typical).
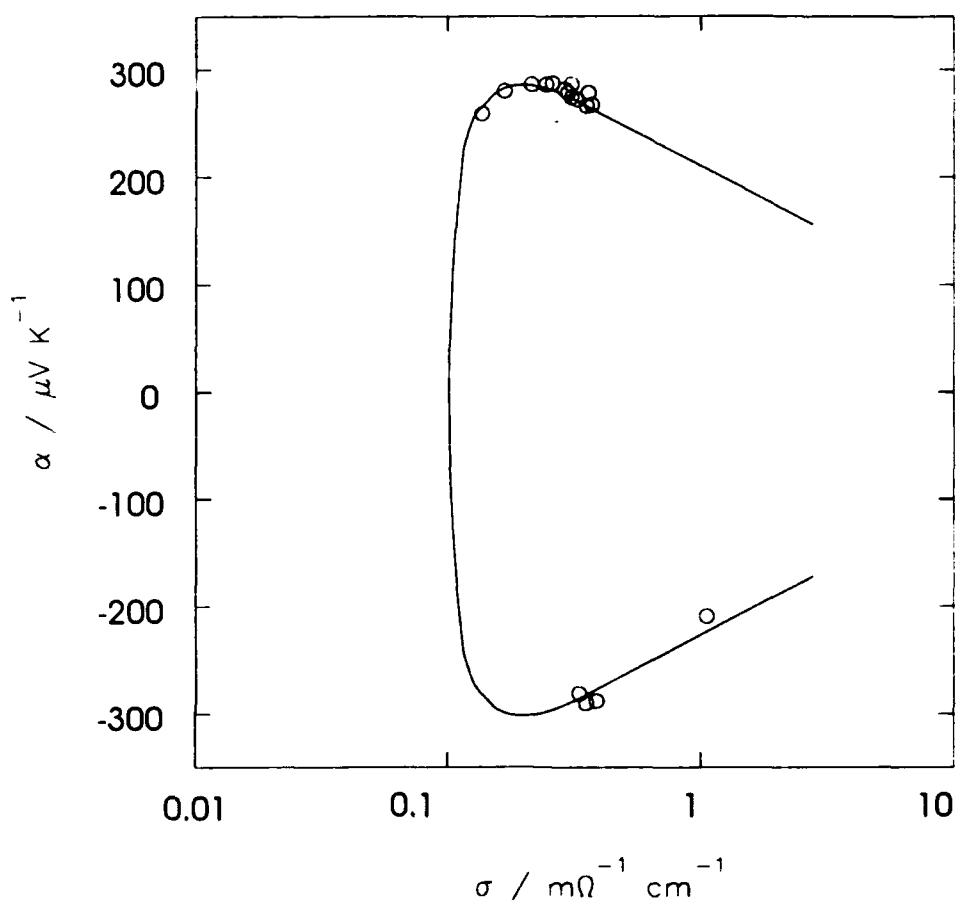
Figure 6. α vs logσ baseline relationship for Br doped Bi_2Te_3-Bi_2Se_3 alloy.

Finally, to demonstrate resonance charge carrier scattering in the Bi-Te-Se alloy, a series of ingots were grown with various combinations of Br and In. Again several samples were taken from each ingot and characterized so that a Jonker plot could be constructed. Table 1 gives the Br and In amounts used.

When resonance charge carrier scattering occurs, the α vs logσ behavior of the material changes. The magnitude of α will increase for a given σ. A Jonker plot would show such points as lying outside the C-shaped baseline α vs logσ curve for the material. The Jonker plot constructed from the data taken from the samples in table 1 is presented in figure 7. Many of the points lie inside the C-shaped baseline curve which was plotted through the points from samples containing no In. These samples inside the curve demonstrate inferior thermoelectric properties to the samples doped with just Br. It is obvious that no data points lie significantly outside of the baseline curve. Thus, the data does not confirm the prediction that In will create resonance charge carrier scattering in Bi_2Te_3-Bi_2Se_3 alloys.

Ingot	In (atomic %)	Br (% of typical)
1	0	1
2	0	2
3	0	5
4	0	10
5	0	20
6	0	50
7	0	100
8	0.01	1
9	0.01	5
10	0.01	20
11	0.01	50
12	0.01	100
13	0.10	1
14	0.10	5
15	0.10	20
16	0.10	50
17	0.10	100
18	1.00	1
19	1.00	5
20	1.00	20
21	1.00	50
22	1.00	100

Table 1. In and Br concentrations surveyed for resonance charge carrier scattering.
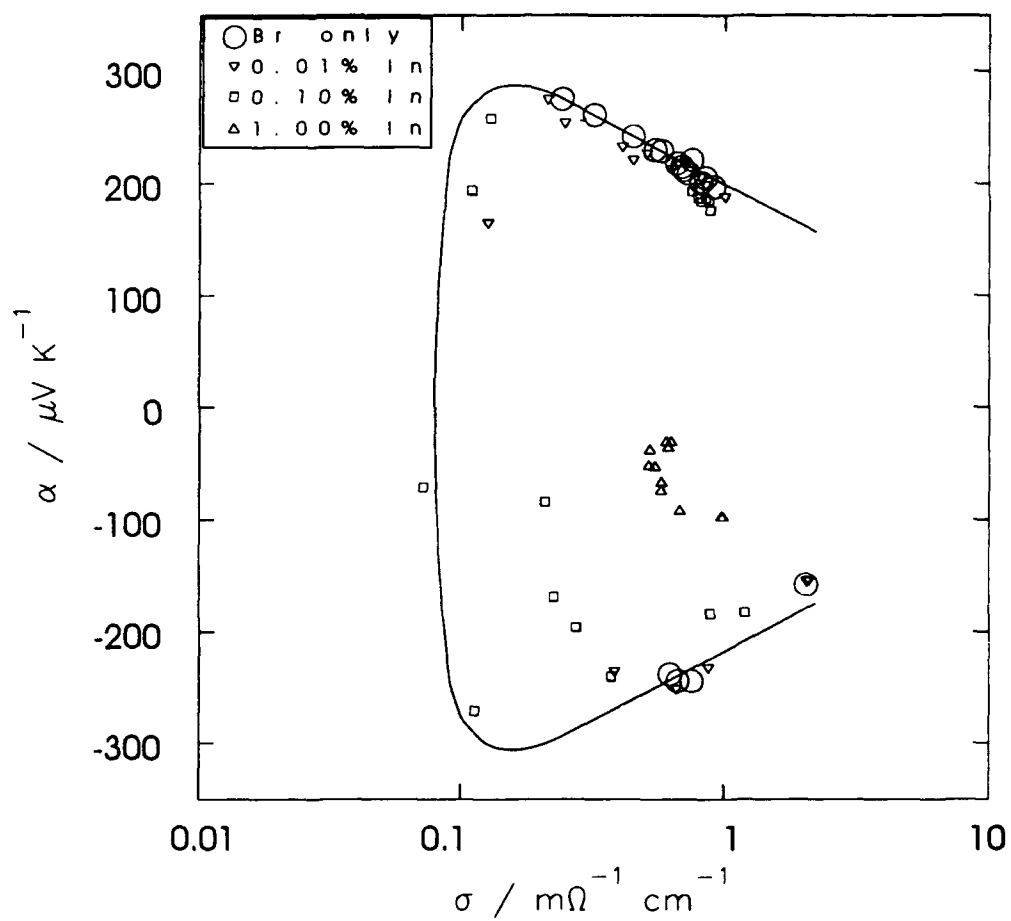
Figure 7. α vs $\log\sigma$ relationship for Br doped Bi_2Te_3-Bi_2Se_3 alloy with In additions. 180 K.

Discussion

While the end result of the Phase I experiments is certainly disappointing, it is informative as well. It is clear that implementation of resonance charge carrier scattering in a thermoelectric material is not a trivial matter. A list of possible explanations for the outcome of Phase I would have to include:

- the theory of resonant charge carrier scattering is invalid
- the impurity chosen, In, does not create useful energy levels
- the energy levels created by In are not useful in the temperature range investigated
- the charge carrier concentrations were not adequate to interact with the impurity energy levels
- the structure and chemistry of the material was not sufficiently controlled

Phase I was executed with the assumption that the theory of resonance charge carrier scattering was valid. A rigorous evaluation of the theory was beyond the scope of this effort. It is certainly possible that the theory is flawed and the improvements reported in PbTe can be attributed to some other factor(s).

Ravich and Vedernikov proposed that In might create resonant energy levels in solid solutions of Bi_2Te_3, Sb_2Te_3 and/or Bi_2Se_3. The suggestion seemed to be based on inferences from referenced work performed on IV-VI compounds and the results of Rosenberg et al. In fact, In might not be capable of creating resonant energy levels in solid solutions of Bi_2Te_3, Sb_2Te_3 and/or Bi_2Se_3 under any conditions.

Even if In does cause the formation of resonant energy states in the Bi-Te-Se alloy, the states might be of no use. If the resonant energy levels are too far from the Fermi energy, then the degree of filling of these levels would be insufficient to enhance α. The Br concentrations used in the experiments may not have positioned the Fermi energy close enough to the impurity energy levels. Temperature also influences the Fermi energy so it is possible that resonance charge carrier scattering could have been observed over some lower or higher temperature regime.

Finally, crystalline or compositional imperfections in the samples produced may have prevented the realization of resonant energy states. It is possible that more elegant techniques, such as molecular beam epitaxy, are necessary to create a Bi-Te-Se alloy which exhibits thermoelectric property improvements through resonance charge carrier scattering.

Phase II Recommendations

The time and funding limitations of Phase I required a relatively straightforward exploration of resonance charge carrier scattering in the Bi_2Te_3, Sb_2Te_3 and/or Bi_2Se_3 system. The results of the experimentation gave no indication whatsoever that the thermoelectric properties of the Bi-Te-Se alloy had been enhanced at any level of σ. Therefore a similar Phase II approach is not recommended. Rather, Phase II should first address the questions brought up in the Discussion above.

First, the theory of resonance charge carrier scattering should be critically reviewed. Examination of the theory might reveal that it is unsupportable. Alternatively the analysis could facilitate the development of a more concise model for predicting those impurities which will create useful energy levels.

As mentioned above, modeling should be used in Phase II to predict whether a given element is likely to generate resonant energy states. The modeling could estimate what carrier concentrations should be used and over what temperature regime resonance charge carrier scattering should be observed. The tight-binding model would utilize possible inputs from the appraisal of resonance charge carrier scattering theory. Inputs would also come from measurements performed to pinpoint the lattice location(s) of the added impurity.

A determination of how the impurity is incorporated into the lattice is important not only for modeling but also to evaluate the ability of a given synthesis technique to achieve the required structure. Measurements would also be performed to determine the actual energy levels created by impurity addition.

Materials would then be synthesized and characterized using the modelling results as a guide. However, if the theory of resonance charge carrier scattering is invalidated or it is proven that resonant energy levels cannot be created in thermoelectric cooling alloys, the Phase II effort would be terminated.

Conclusions

Ravich and Vedernikov reviewed the improvement in thermoelectric properties achieved in PbTe upon the simultaneous addition of Na and Tl. This improvement is attributed to resonance charge carrier scattering which increases Z primarily because of an increase in α relative to σ.

The objective of Phase I was to invoke resonance scattering of charge carriers in a Bi_2Te_3 based thermoelectric cooling alloy. The work was performed using a Br doped Bi-Te-Se alloy. Based on the review of Ravich and Vedernikov, In was selected as the impurity element to create the resonant energy levels.

The baseline relationship between α and σ, for the Bi-Te-Se alloy, was determined by varying the Br concentration. Various levels of In, all below the experimentally determined solubility limit, were then combined with different Br levels in the thermoelectric alloy. Jonker plot analysis of the characterized samples gave no indication that α had been enhanced for any σ. No evidence was found to suggest that resonance charge carrier scattering occurred in any of the samples.

There are several possible explanations for the results. The theory might not be valid or In may not be capable of creating useful energy levels in the alloy investigated. The problem may have been insufficient carrier concentrations to activate the resonant states or the measurements were not carried out over the right temperature range. The logical Phase II approach would examine these issues rigorously before making more materials.

Phase II would critically examine the theory of resonance charge carrier scattering. Modelling would be used to select impurity elements likely to create useful energy levels in the band structure of the Bi_2Te_3 based alloys. Measurements would be performed to determine actual energy levels created by impurity additions and determine how the impurity is incorporated into the atomic lattice. Information from the modeling and the above measurements would be used to maximize the probability of utilizing resonance charge carrier scattering to improve the thermoelectric properties of Bi_2Te_3 based alloys.

Endnotes

1. Ravich, V. I., Vedernikov, M. V., *Proceedings of the IX International Conference on Thermoelectrics*, Pasadena, CA, 278, 1990

2. Rosenberg, A. J., Strauss, A. J., *J. Phys. Chem. Solids*, **19**, 105, 1961

3. Horak, J., Stary, Z., Lostak, P., Pancir, J., *J. Phys. Chem. Solids*, **51**, 1353, 1990